

Optical spectra and exchange-correlation effects in molecular crystals

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We report first-principles GW-Bethe Salpeter Equation and Quantum Monte Carlo calculations of the optical and electronic properties of molecular and crystalline rubrene ($C_{42}H_{28}$). Many-body effects dominate the optical spectrum and quasi-particle gap of molecular crystals. We interpret the observed yellow-green photoluminescence in rubrene microcrystals as a result of the formation of intermolecular, charge-transfer spin-singlet excitons. In contrast, spin-triplet excitons are localized and intramolecular with a predicted phosphorescence at the red end of the optical spectrum. We find that the exchange energy plays a fundamental role in raising the energy of intramolecular spin-singlet excitons above the intermolecular ones. Exciton binding energies are predicted to be around 0.5 eV (spin singlet) to 1 eV (spin triplet). The calculated electronic gap is 2.8 eV. The theoretical absorption spectrum agrees very well with recent ellipsometry data.

Organic molecular crystals are promising semiconductor materials for applications in light-emitting devices, solar cells, and electronics. Owing to the weak intermolecular interactions, transport and photo-excitation in organic crystals deviate from those of inorganic solids with covalent or ionic bondings [1, 2]. Extrinsic factors such as structural imperfections and trap states have long posed a challenge for experimental investigation of organic molecular crystals, although recent success in fabricating organic single crystal field-effect transistors has helped to reveal intrinsic charge transport [3]. Moreover orders of magnitude higher mobilities than in the organic thin films or polymers have been obtained. In particular, the rubrene single crystal has demonstrated the highest mobility [4]. Currently, spectroscopy experiments including transient absorption, luminescence, and photo-current spectroscopy have revealed dominant excitonic effects in the optical response of the rubrene crystal [5, 6, 7, 8]. Interpretations of the spectrum, however, have been complicated by environmental factors such as oxidation of the rubrene surface [8, 9].

On the theoretical level, a basic understanding of photo-excitations and quasi-particle gaps of a rubrene crystal is lacking. Only limited *ab initio* band structure calculations within local-density (LDA) or generalized-gradient approximation (GGA) of density-functional theory (DFT) of rubrene have been reported [10, 11]. The LDA and GGA are known to fail in describing electron-hole and electron-electron interaction which are responsible for the formation of excitons and the quasi-particle gap [12, 13]. An *ab initio* study of the quasi-particles and their interaction with light in a molecular crystal must include those effects. However, complexity has hindered the use of theories beyond DFT. We have only recently met this challenge by a combination of advanced algorithms and parallel computers.

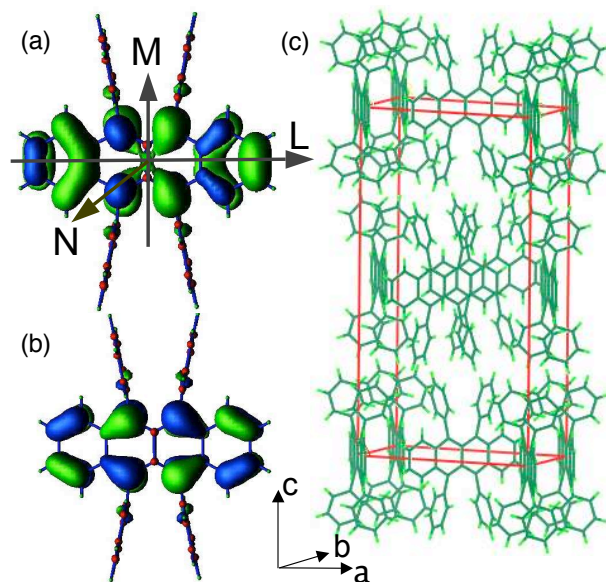


FIG. 1: LUMO (a) and HOMO (b) isosurfaces in a rubrene molecule. The tetracene backbone is on the plane of the figure. Green and blue colors denote positive and negative values. (c): Schematic view of the rubrene crystal.

In this letter, we demonstrate the possibility of *ab initio* calculation of excitations including correlation and excitonic effects in technologically relevant molecules such as rubrene. We find that the exchange interaction plays a fundamental role in determining the properties of excitations in this material.

Our approach consists of four steps: i) The ground state structures and the electronic wavefunctions of the system are described within pseudopotential DFT-GGA; ii) we calculate quasi-particle energies within the GW approximation, which includes many-body effects in the electron self-energy [12]; iii) the optical excitations are

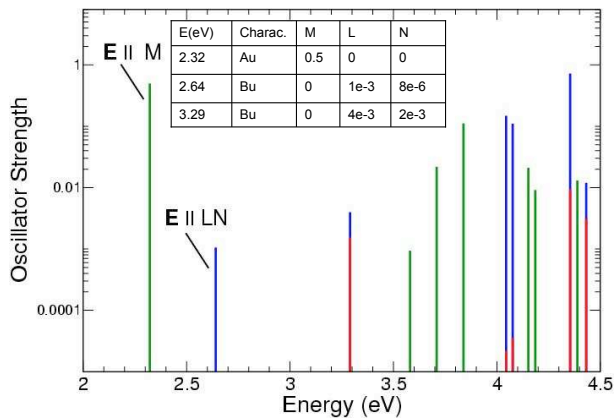


FIG. 2: Calculated oscillator strength of the first few optical transitions in gas-phase rubrene. The inset shows the excitation energies, group symmetry characters, and oscillator strengths of the three lowest excitations.

obtained by solving the Bethe-Salpeter equation (BSE) for electrons and holes [13] and finally, iv) we assess the validity of the GW-BSE methodology by comparing its prediction of ionization potential and the first spin-triplet excitation with diffusion Quantum Monte Carlo (QMC) calculations [15].

We start by exploring the electronic properties of individual rubrene molecules. The isolated molecule has C_{2h} symmetry. It consists of 4 phenyl groups attached to a tetracene backbone. Fig. 1 shows isosurfaces of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the molecule. L , M , and N denote the long, short and normal axes of the tetracene backbone, respectively. HOMO – LUMO electronic dipole transitions along directions L and N are dipole-forbidden. The lowest dipole-allowed transition is polarized along the M axis.

Within the GW approximation for finite systems [22], the ionization energy E_I and the electron affinity E_A for the isolated rubrene molecule are respectively 6.30 eV and 1.88 eV. Independent diffusion QMC calculations [15] give $E_I \sim 6.22 \pm 0.14$ and $E_A \sim 0.96 \pm 0.14$ eV. The calculated ionization energies compare well with 6.4 eV from the ultraviolet photo-electron spectroscopy [14], which validates the method for this system. The overestimation of electron affinity within the GW approximation compared with QMC has been also observed in fullerenes in gas phase [21]. The accuracy of energy gaps calculated within the GW approximation seems to be much better in organic solids [18, 23].

Absorption lines obtained within the BSE are shown in Fig. 2. The first absorption line is at 2.32 eV, polarized along the M axis. This is in good agreement with the experimental absorption peak at 2.35 eV of the rubrene molecule in solution [7]. The next absorption line is at 2.6 eV, polarized in the LN plane. Both excitation en-

ergies obtained from our calculations are ~ 0.5 eV lower than those calculated by semi-empirical methods [7]. At higher energy, there is an intense absorption line at 4.35 eV, consistent with experimental data (4.1 eV) [16] and semi-empirical calculations (4.48 eV) [7].

To characterize better the electronic states contributing to the excitons, we project the BSE eigenvectors onto each energy band. The first excitation is dominated by the transition between the HOMO and LUMO with about 89% weight. The remaining 11% comes from energy levels further away from the HOMO-LUMO gap. The second BSE excitation is strongly mixed, with components involving the 7 highest occupied energy levels and ~ 11 unoccupied levels. The HOMO-(LUMO+1) transition itself contributes only 30% to this excitation. Besides the spin-singlet states in the absorption bands, spin-triplet states which are dipole-forbidden can also be obtained. The excitation energy is lower for the triplet, as a result of absent exchange repulsion among electrons and holes. From GW/BSE, we have obtained an excitation energy of 0.8 eV for the first triplet state, which should be compared with 1.45 ± 0.13 eV predicted from our QMC calculations. The discrepancy of 0.65 eV originates from the difference in the electron affinity calculated by the two different methods.

Rubrene crystallizes in an orthorhombic structure with lattice parameters $a = 14.4$ Å, $b = 7.2$ Å, and $c = 26.8$ Å [17]. Each unit cell contains two staggered ab planes separated by $c/2$. Each plane contains two translationally inequivalent rubrene molecules arranged in a herringbone structure (see Fig. 1c). Across planes, the molecules are bonded by weak forces. As a result, the electronic properties of the material are not sensitive to the exact stacking of layers. Therefore, we have modeled the orthorhombic crystal with equivalent ab planes separated by approximately 14.4 Å, keeping the same geometry along the ab plane. This inter-planar distance preserves weak chemical bonds across neighbor planes and similar dielectric screening as in the staggered stacking, thus ensuring equivalent electronic properties between the model crystal and the crystal as characterized by X-ray measurements [17]. We obtained a DFT-GGA band gap of 1.20 eV for the model unit cell and 1.14 eV for the experimental structure [17]. We also calculate the diagonal components of the static dielectric tensor ϵ_∞ within the random phase approximation (RPA), obtaining 2.55, 2.83 and 3.12 for a , b and c polarizations respectively. Spectroscopic determinations for these quantities are: 2.6, 3.2 and 2.2 [7] for a , b , and c polarizations (2.15, 2.4 for a and b [10]) respectively [24]. The agreement with results from the experimental structure [17] demonstrates that the model unit cell is sufficient for evaluating the quasi-particle energies and the excitons. The small difference along c is a consequence of the reduced unit cell.

In the framework of the BSE method, we calculate the imaginary part of dielectric functions from the optical

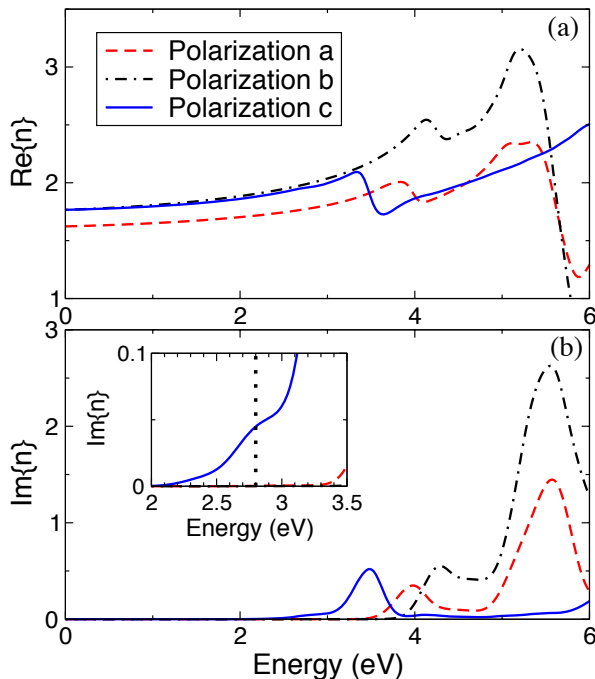


FIG. 3: Real (a) and imaginary (b) parts of the refractive index along the crystalline axes of the rubrene crystal. The vertical line in the inset marks the GW quasiparticle gap.

transition matrix:

$$\epsilon_2(\omega) = \frac{4\pi^2 e^2}{\omega^2} \sum_S \left| \sum_{v,c} A_{vc}^S \langle v | \vec{\lambda} \cdot \vec{V} | c \rangle \right|^2 \delta(\omega - \Omega_S) \quad (1)$$

where v, c are the single-particle valence and conduction states, \vec{V} is the velocity operator, $\vec{\lambda}$ is the polarization of light, Ω_S are the excitation energies of the excited states S in the crystal, and A_{vc}^S are the expansion coefficients of the excited states in electron-hole pair configuration $|S\rangle = \sum A_{vc}^S a_c^\dagger a_v |0\rangle$. The expansion coefficients are obtained as eigenvectors of the effective Hamiltonian in the BSE. Detailed formalism and technique are described in [13]. We apply a $4 \times 8 \times 4$ sampling of the Brillouin zone and solve the BSE equations for 8 valence and 8 conduction bands. The real part of the dielectric function is a Kramers-Kronig continuation of Eq. (1). Finally, the refractive index is obtained as $n = \sqrt{\epsilon_1 + i\epsilon_2}$.

We neglect the effect due to electron-phonon coupling in this work as the excitonic effect arising from purely electronic orbitals is our main concern. The approximation is justified by a recent study of the effective masses of carriers in rubrene crystal field effect transistor which showed that the dominant excitations are quasiparticles rather than polarons [10]. It is also corroborated by the spectroscopy data which suggested that primary excitons in rubrene crystals are free excitons which do not involve lattice vibrations [5].

The imaginary part of the refractive index along all three crystalline directions of the rubrene crystal is shown

in Fig. 3b. The first exciton line is at 2.3 eV, polarized along the c axis. Above it, there is a series of bound excitons with the same polarization, forming a flat “hump” at the onset of photo-absorption (see inset of Fig. 3). This exciton band should be associated to the first singlet level of the rubrene molecule coming from the HOMO-LUMO molecular transition and it is in good agreement with the experimentally determined absorption onset [5, 7, 8]. The oscillating features in the experimental spectra correspond to vibrational resonance which is not included in the present theory. Tavazzi *et al.* [7] have reported weak absorption peaks around 2.5 eV in the ab plane and attributed them to the second singlet of rubrene molecule in the LN plane. This interpretation is not supported by our results. We find no remarkable oscillator strength around this energy with in-plane polarizations. Indeed, our results for the rubrene molecule show that the second singlet is two orders of magnitude weaker than the first one. The absorption lines reported at 2.5 eV in the ab plane could also be enhanced by crystal imperfections or coupling to phonon bands, effects which are not included in our study. Our calculations further show absorption peaks at about 3.9 and 4.1 eV while the experimental peaks appear at about 3.7 and 4.0 eV along a and b axes, respectively.

The real part of the refractive index is shown in Fig. 3a. A pronounced anisotropy can be seen with enhanced response along the b axis, in agreement with experiment [7, 10]. For the a and b polarizations, diagonal components of the static dielectric tensor are found to be 2.62 and 3.1, larger than the values we obtained using the random phase approximation (RPA) and closer to those obtained from experiment [7]. Our GW-BSE value is larger than the measured one along c [7], for the same reason as in the RPA calculations discussed earlier.

The GW approximation predicts a quasi-particle band gap of about 2.8 eV, increased from the DFT-GGA gap of 1.2 eV [10]. The difference between this gap and the calculated excitation energies gives rise to a binding energy of 0.5 eV for the first singlet exciton. The binding energy of the first exciton is comparable to those reported for pentacene (0.3-0.5 eV [18]) an tetracene (0.4 eV [20]). No direct measurements of the electronic gap of rubrene crystal could be found in the literature. Furthermore, there is evidence that photo-excitation does not create uncorrelated electron-hole pairs directly [5], suggesting it is difficult to directly measure the electronic gap without pulling electrons and holes apart. This behavior is typical of tightly bound excitons. Our study, combined with the experiments, thus allow us to provide additional information on the underlying band structure of rubrene.

Spin-triplet excitons are not accessible in optical absorption experiments, nevertheless they play a fundamental role in emission processes such as phosphorescence [1]. The long life-time of triplet excitons is a consequence of the electron and hole having parallel spins. This also

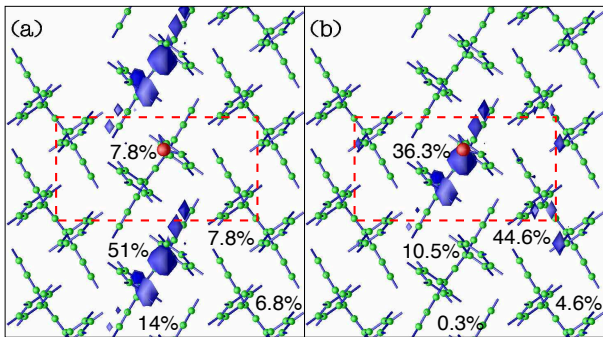


FIG. 4: Electron-hole probability distributions of the first spin-singlet (a) and spin-triplet (b) excitons of rubrene crystal. Red dot in the center of the unit cell (viewed along c axis) marks the hole while the isosurfaces indicate the distribution of the electron. The probabilities for finding the electron on each molecular site are indicated by the percentage.

cancels out the exchange repulsion, raising the binding energy. The first spin-triplet exciton in organic molecular crystals is often a molecular exciton with very high binding energy [18, 19]. Rubrene is not an exception. The triplet has excitation energy 1.4 eV, close to the QMC excitation energy of the first triplet exciton in gas-phase rubrene. Fig. 4 shows that the first triplet exciton is a fairly well-defined molecular exciton, i.e., electron and hole have a 36% probability of being found at the same molecular site.

In contrast, the probability of electron and hole being at the same molecular site is just 8% for the singlet (Fig. 4a). The electron and hole are primarily distributed over second neighbor molecular sites, separated by approximately 7 Å [25] indicating it is a charge-transfer exciton. Excitons in the 2.3-2.9 eV range shown in Fig. 3 are also charge-transfer states but of larger size. The exchange repulsion prevents the first spin singlet from being intramolecular. The exchange repulsion is 2 eV when electron and hole are on the same site but drops to less than 0.1 eV when electron and hole are on neighbor sites, owing to its short range. This drop compensates the drop in Coulomb attraction between the on-site (2 eV) and the off-site configuration (1 eV). As a result, an intramolecular spin-singlet exciton would be more energetic than the first charge-transfer one by approximately 1 eV. This interpretation is supported by our gas-phase calculations: assuming that the GW electron affinity is overestimated by 0.6 to 0.9 eV, as indicated by QMC, we estimate the excitation energy of intramolecular spin-singlet exciton to be ~ 3 eV, i.e., 0.7 eV higher than the first charge-transfer exciton.

To conclude, we have studied the electronic excitations and optical spectra of crystalline and molecular rubrene from first-principles approaches including both electron self-energy corrections and electron-hole correlations. We find the lowest dipole-allowed exciton at around 2.3 eV,

both for the molecule and the crystal, thus confirming the experimental absorption energies. These excitons are spin-singlets and originate from transitions between the HOMO and LUMO. We also achieved good agreement in the reflectance spectrum. The spatial distribution of the spin-singlet and triplet excitons are analyzed and compared for the rubrene crystal. We have shown that the optical spectrum and quasi-particle gap are strongly affected by many-body effects. Thus, the results reported here are key to understand the electronic structure of the rubrene crystal. Charge-transfer and molecular excitons might exist in other molecular crystals [18, 20] and arrays of quantum dots. Moreover, charge-transfer excitons depend on the local crystalline structure, therefore we predict a high sensitivity of the optical spectrum to pressure-induced phase transitions in this material.

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 - [24] We follow the axes notation used in Ref. [10].
 - [25] Using $-e^2/\epsilon r$ with an average dielectric constant $\epsilon \sim 2.5$ and the interatomic distance $r = 7 \text{ \AA}$, we obtain a binding energy of 0.8 eV, slightly larger than the GW/BSE value.